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On Electron Attachment to HBO_2

Aerophysics Laboratory
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30 December 1976

Interim Report

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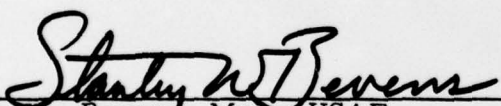
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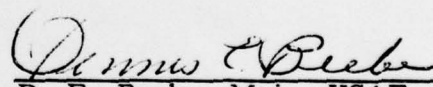
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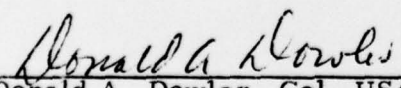
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1. INTRODUCTION

Miller and Gould recently reported [4] measurements in which well-characterized laboratory test flames were seeded with KNO_3 and H_3BO_3 . They assume that H_3BO_3 is rapidly converted within these flames to HBO_2 . The potassium in KNO_3 ionizes, producing free electrons. They studied the reaction



by measuring at various positions in the flame $[e^-]$, $[\text{H}]$ and $I(\text{BO}_2^-)$, where $I(\text{BO}_2^-)$ is related to $[\text{BO}_2^-]$ via

$$[\text{BO}_2^-] \approx S \cdot I(\text{BO}_2^-) \quad (2)$$

S is the sensitivity of the mass spectrometer which must be determined experimentally. S varies from flame to flame and from day to day but, in any given flame on any particular day, is constant at all points in the flame. Miller and Gould conclude from their measurements that at most locations in the flame reactions 1 and -1 are not equilibrated, that is to say $k_1[e^-][\text{HBO}_2] \neq k_{-1}[\text{H}][\text{BO}_2^-]$ and that the data are consistent with a rate coefficient for reaction 1, (k_1), equal to $3.2 \times 10^{-10} \exp -11000/T \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$.

In this letter, the data are reanalyzed. It is shown that the data are also consistent with the premise that reactions 1 and -1 are equilibrated and that k_1 is greater than the value deduced by Miller and Gould.

2. ANALYSIS

First, let us review the method of analysis used by Miller and Gould. They assume that the rate of change of $[\text{BO}_2^-]$ is due only to reaction 1 and is given by the expression

$$\frac{d[\text{BO}_2^-]}{dt} = k_1[e^-][\text{HBO}_2] - k_{-1}[\text{BO}_2^-][\text{H}] \quad (3)$$

Miller and Gould determined k_1 from Eqs. (2) and (3) by finding values of k_1 and S that satisfy these equations at various positions in the flame [$k_{-1} = k_1/K_1(T)$, where $K_1(T)$ is the equilibrium constant]. They take the temperature of the flame and hence k_1 to be constant; they conclude that diffusion is unimportant and assume that the conversion of H_3BO_3 to HBO_2 is complete at all positions in the flame where measurements were made. Miller and Gould find from such an analysis that $k_1 = 3.2 \times 10^{-10} \exp -11000/T \text{ cm}^3/\text{s}$. There is nothing wrong, in principle, with this method of analysis. It is limited only by the precision of the data and the accuracy of the assumptions employed. Miller and Gould hence are correct in stating that their measurements are consistent with the value they report for k_1 .

The thesis of this letter is that the data of Miller and Gould are also consistent with the premise that reactions 1 and -1 are equilibrated in the flames studied. If these reactions are equilibrated, the following relation holds:

$$k_1[e^-][\text{HBO}_2] = k_{-1}[\text{H}][\text{BO}_2^-] \quad (4)$$

or

$$\frac{[\text{H}][\text{BO}_2^-]}{[e^-][\text{HBO}_2]} = \frac{k_1}{k_{-1}} = K_1(T) \quad (5)$$

Substitution of Eq. (2) into Eq. (5) yields

$$\frac{[H] \cdot I(BO_2^-)}{[e^-]} = \frac{K_1(T)[HBO_2]}{S} \quad (6)$$

In any particular flame, $K_1(T)$ and S are roughly constant, and if we assume (as do Miller and Gould) that H_3BO_3 is rapidly converted to HBO_2 , then $[HBO_2]$ and consequently the right hand side of Eq. (6) will be roughly constant. Equilibrium then implies constant values for $[H] \cdot I(BO_2^-)/[e^-]$. Table 1 gives the values of $[H] \cdot I(BO_2^-)/[e^-]$ at various positions in the two flames for which data were reported. Except for the first cm or two of the low pressure flame, $[H] \cdot I(BO_2^-)/[e^-]$ is indeed constant within the limits of experimental accuracy.

In Figures 1 and 2, $[BO_2^-]_{eq}$ and $[BO_2^-]_m$ are plotted as a function of distance from the burner. $[BO_2^-]_{eq}$ is the equilibrium value of $[BO_2^-]$ as computed from Eq. (5). $[BO_2^-]_m$ is the measured value of $[BO_2^-]$ as computed from Eq. (2). The values used for the sensitivity of the mass spectrometer, S , were computed from Eq. (6) and the results of Table 1. In Figures 1 and 2, the measured values of $[BO_2^-]$ are approximately equal to the equilibrium values except for the first cm or two in the low-pressure flame. Although the deviation in the low pressure flame might be due to the slowness of reaction 1, it might equally well be due to the slowness in the conversion of H_3BO_3 to HBO_2 , or may even be due to experimental error. Experimental measurements in this region are prone to error. The mass spectrometer used to measure BO_2^- concentrations has a larger diameter than does the flame, thereby causing significant perturbations in the flame aerodynamics. Over a distance of 1 cm in the low-pressure flame, $[BO_2^-]$ changes by about an order of magnitude; even under the best of conditions it would be difficult to accurately measure such a rapidly varying profile. Similar difficulties may also occur in the measurement of $[e^-]$. A microwave cavity is employed that has a depth (and hence a resolution) of 0.3 cm. It is difficult,

Table 1. Consistency of Data with the Assumption of Equilibrium

A. 100 torr flame ($\text{H}_2/\text{O}_2/\text{N}_2 = 2.5/1.0/3.0$), $T = 1980\text{K}$

distance from burner (cm)	$I(\text{BO}_2^-)[\text{H}]/[\text{e}^-]$ (A)
2	1.5×10^{-5}
4	1.6×10^{-4}
6	1.8×10^{-4}
8	1.8×10^{-4}
10	1.9×10^{-4}
12	1.9×10^{-4}
14	1.8×10^{-4}
16	1.8×10^{-4}

B. 1 atm flame ($\text{H}_2/\text{O}_2/\text{N}_2 = 3.5/1.0/3.0$), $T = 2250\text{K}$

distance from burner (cm)	$I(\text{BO}_2^-)[\text{H}]/[\text{e}^-]$ (A)
1.0	1.4×10^{-6}
1.5	2.2×10^{-6}
2.0	2.3×10^{-6}
2.5	2.0×10^{-6}

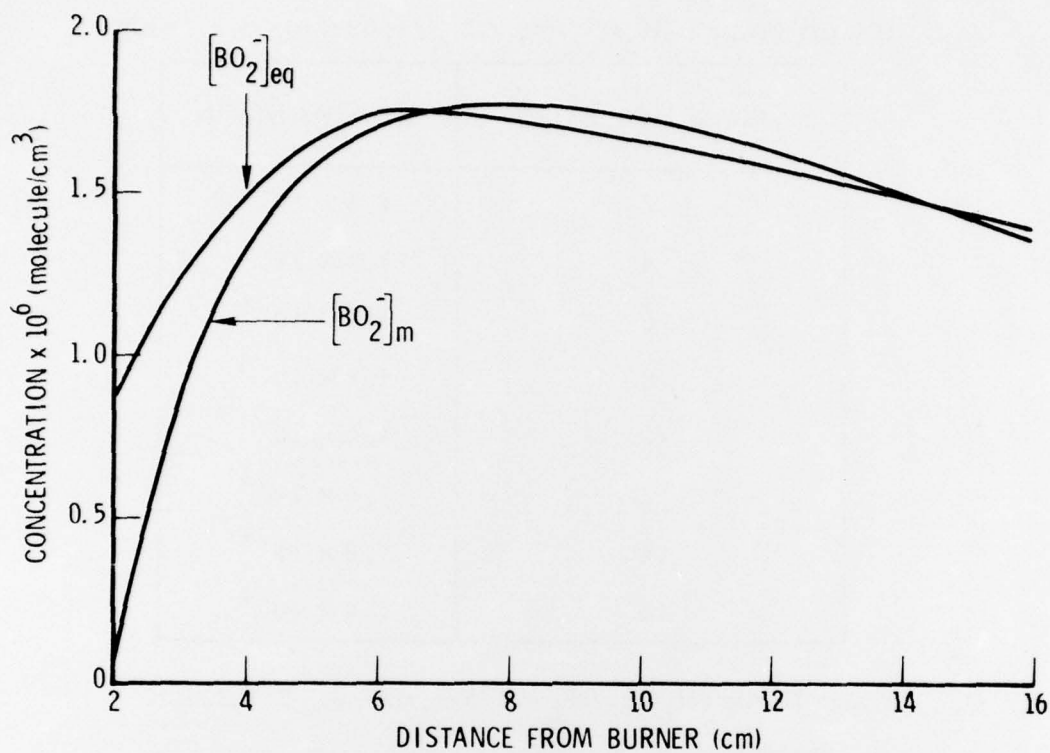


Fig. 1. 100 torr flame. $[\text{HBO}_2] = 7 \times 10^{10} \text{ cm}^{-3}$, $S = 3.7 \times 10^{15} \text{ A}^{-1} \text{ cm}^{-3}$; $[\text{BO}_2^-]_{\text{m}}$ is the measured concentration of BO_2^- , $[\text{BO}_2^-]_{\text{eq}}$ is the equilibrium concentration.

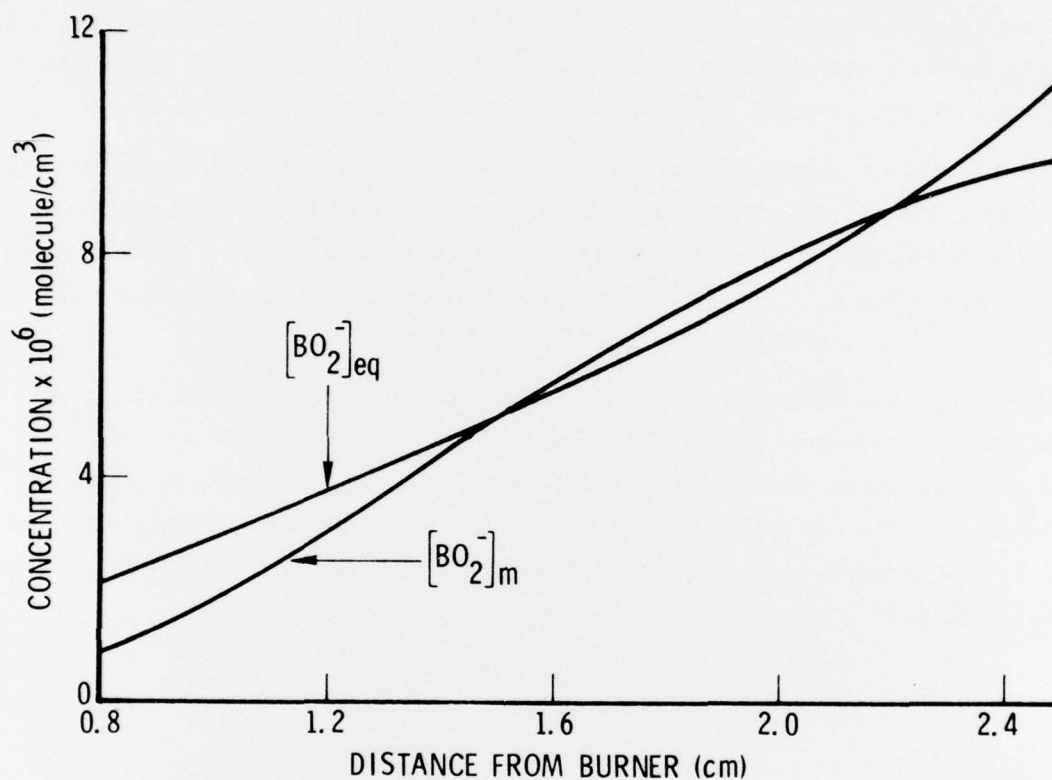


Fig. 2. 1 atm flame. $[\text{HBO}_2] = 3 \times 10^{11} \text{ cm}^{-3}$, $S = 2.4 \times 10^{18} \text{ A}^{-1} \text{ cm}^{-3}$; $[\text{BO}_2^-]_{\text{m}}$ is the measured concentration of BO_2^- , $[\text{BO}_2^-]_{\text{eq}}$ is the equilibrium concentration.

without employing deconvolution techniques, to obtain accurate profiles of $[e^-]$ if $[e^-]$ is also varying rapidly.

It seems that, in spite of the discrepancies in the first centimeter or two of the low-pressure flame data, it is reasonable to conclude from the results in Table 1 and Figures 1 and 2 that the data of Miller and Gould are consistent with the premise that reactions 1 and -1 are equilibrated.

Numerical calculations were performed using Eq. (3) and the measured values of $[H]$ and $[e^-]$ for different values of k_1 . It was found that reaction 1 is essentially equilibrated in the 1980K flame for $k_1 \geq 2 \times 10^{-12} \text{ cm}^3/\text{s}$ and in the 2250K flame for $k_1 \geq 5 \times 10^{-11} \text{ cm}^3/\text{s}$. Miller and Gould conclude that $k_1 = 1.1 \times 10^{-12}$ at 1980K and 2×10^{-12} at 2250K.

Numerical calculations also show, for the 2250K flame, that reaction 1 is not equilibrated even at a distance of 2.4 cm if k_1 is as low as 2×10^{-12} . The only way to make measurements and calculations agree with $k_1 = 2 \times 10^{-12}$ is to choose a value for S that is one-half of the value used in the calculations of Fig. 2, which leads to the result that in this flame $[BO_2^-]/[BO_2^-]_{eq}$ is always equal to about 0.5.

3. DISCUSSION

The data of Miller and Gould are amenable to two different interpretations. More experiments are needed to establish which interpretation is the better.

The interpretation given by Miller and Gould is essentially a two-parameter fit to the data (k_1 and S variable) while the interpretation given here is a one parameter fit (S , only, variable). It should be mentioned that the interpretation of Miller and Gould gives a closer match between measurement and calculation. But this should not be a surprising result, for in general a two-parameter fit yields a closer match than does a one-parameter fit.

Even though only further experimentation can decide the correct value of k_1 , I favor the interpretation drawn herein for two reasons.

First, Miller and Gould [2] have recently studied electron attachment to HCl using the same flames as were used in the HBO_2 studies. They analyzed their data in the same way and found what appear to be anomalously small values for the rate of electron attachment which are in disagreement with other measurements. This suggests that flame data might not be accurate enough to warrant an analysis involving two adjustable parameters.

Second, if k_1 is based on the value derived by Miller and Gould, the rate coefficient for reaction 1, as calculated from the relationship $k_{-1} = k_1/K_1$ is not in accord with expectations based on reaction-rate theory. Jensen [3] found

$$K_1 = 1500 \exp -10000/T \quad . \quad (7)$$

This measurement has been confirmed by Srivastava et al. [4]. Hence,

$$k_{-1} = \frac{3.2 \times 10^{10} \exp(-11000/T)}{1.5 \times 10^3 \exp(-10000/T)} = 2 \times 10^{-13} \exp(-1000/T) \quad (8)$$

This rate coefficient has an unusually small preexponential factor. According to a formula first derived by Langevin [5], if reaction -1 occurs every collision, its rate coefficient would be $2 \times 10^{-9} \text{ cm}^3/\text{s}$ independent of temperature. The preexponential factor in Eq. (8) implies a steric factor of $(2 \times 10^{-13}) / (2 \times 10^{-9}) = 10^{-4}$. That is to say only 1 out of 10^4 collisions energetic enough to cause reaction actually do so. I know of no theory capable of explaining such a small steric factor. Thus, either the value chosen by Miller and Gould for k_1 is incorrect or conventional thinking about reaction rates must be modified.

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